PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-064927
(43)Date of publication of application : 08.03.1994

(51)Int.Cl. C01G 49/06
H01F 1/11

(21)Application number : 03-359299
(22)Date of filing : 27.12.1991

(71)Applicant : TODA KOGYO CORP
(72)Inventor : NAKAMURA TATSUYA
HONNA TORAYUKI

(54) PRODUCTION OF ACICULAR HEMATITE PARTICLE POWDER

(57)Abstract:
PURPOSE: To provide a process for the industrial production of an essentially high-density acicular hematite particle having improved crystallinity while keeping the acicular form of the starting material.
CONSTITUTION: The objective acicular hematite particle having an average major axis diameter of 0.1-0.5gm and a specific surface area of 15-60m2/g measured by BET method can be produced by heating and dehydrating acicular goethite particle at 250-400°C to obtain acicular hematite particle having an average length of 0.1-0.5μm and a specific surface area of 70-150m2/g measured by BET method and subjecting an aqueous dispersion containing the hematite particles to hydrothermal treatment at 150-250°C.

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]Average length shaft length produced by carrying out heating drying of the needlelike goethite particles in a 250-400 ** temperature requirement is 0.1-0.5 micrometer, And when specific surface area by a BET adsorption method carries out water heat treatment of the aquosity solvent containing a needlelike hematite particle which is 70-150m^2/g in a 150-250 ** temperature requirement, A manufacturing method of acicular hematite particle powder characterized by a thing for which the shape of a needle whose specific surface area by a BET adsorption method is 15-60m^2/g whose average length shaft length is 0.1-0.5 micrometer is inherited, and which obtain a high-density needlelike hematite particle substantially.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the manufacturing method of the acicular hematite particle powder as a starting material at the time of manufacturing the magnetic particle powder for magnetic recording.
It aims at the thing for which maintenance succession of the acicular shape is carried out, and the crystalline degree inside a particle surface and particles was raised in detail and which obtain high-density acicular hematite particle powder substantially.

[0002]
[Description of the Prior Art]The necessity for highly-efficient-izing over magnetic recording media, such as magnetic tape and a magnetic disk, is arising increasingly as the small weight saving of the apparatus for magnetic-recording playback progresses in recent years. That is, improvement in various characteristics, such as a high density recording characteristic, the high-output characteristic, the high sensitivity characteristic, and a frequency characteristic, is demanded, and, for that purpose, high-coercive-force-izing of a magnetic recording medium and improvement in the residual magnetic flux density Br are required.
[0003]For high-coercive-force-izing of a magnetic recording medium, it is required for magnetic particle powder to have high coercive force. It depends for the residual magnetic flux density Br of a magnetic recording medium on the dispersibility in the inside of the vehicle of magnetic particle powder, the stacking tendency in the inside of a coat, and restoration nature, and magnetic particle powder is a needlelike gestalt.
Sintering does not occur between particles, and a hole does not exist in the inside of a particle surface and particles, but it is required to be high density substantially.

[0004]Now, needlelike magnetite particle powder and needlelike maghemite particle powder are mainly used as magnetic particle powder for magnetic recording. These magnetic particle powder carries out air oxidation of the ferrous hydroxide colloid in the solution generally obtained by making a ferrous salt aqueous solution and alkali react (usually). It is called a wet reaction. Near 300 ** in the air, carry out heating drying and the obtained needlelike goethite particles A needlelike hematite particle and nothing, Furthermore, hydrogen etc. are returned at 300-400 ** among reducing gas, and it is considered as needlelike magnetite particles, and is obtained by oxidizing at 200-300 ** among the air, and subsequently, making this into needlelike maghemite particles.
[0005]An expression of relations as shown below can express the coercive force Hc of magnetic particle powder.
Hc=K -(Nb-Na)- Ms -- in this expression of relations -- K -- the crystalline degree of particles -- (Nb-Na) -- the shape (needlelike nature) of particles -- Ms is a matter related to the chemical

presentation of particles. In order to aim at improvement in the coercive force of magnetic particle powder so that clearly from this expression of relations, it is required that maintenance succession of the acicular shape of needlelike goethite particles is carried out and that a crystalline degree should be raised. And the various characteristics of these magnetic particle powder are required not only the improvement in coercive force but in order to raise the dispersibility in the inside of the vehicle of magnetic particle powder, the stacking tendency in the inside of a coat, and restoration nature.

[0006]In order to carry out maintenance succession of the acicular shape of goethite particles in manufacture of magnetic particle powder conventionally as mentioned above, carrying out heating drying at low temperature comparatively is performed. Thus, on the other hand, it consists of floc which many single particles connected, and since this skeleton particle does not have the enough particle growth of this single particle, a crystalline degree is small [a particle], although the obtained needlelike hematite particles are needlelike skeleton particles which left the outside of needlelike goethite particles.

[0007]If a crystalline degree carries out heating reduction, using a small needlelike hematite particle as a starting material, Since it is rapid in a heating reduction process, the particle growth, i.e., the physical change, of a single particle, in the portion in which the uniform particle growth of the single particle did not occur easily, therefore the particle growth of the single particle occurred rapidly, particles and sintering between particles occur and particle shape collapses easily.

[0008]Although needlelike goethite particles contain inevitably impurities originating in raw materials, such as NaOH and $FeSO_4$, such as Na^+ and SO_4^{2-}, In order that these impurities may promote sintering in a heating firing process, when the needlelike goethite particles which contain these impurities so much are used, in a heating reduction process, particles and sintering between particles occur much more easily, and particle shape collapses easily.

[0009]The particle growth of a single particle does not occur in the heating oxidation process in which needlelike magnetite particles are made into needlelike maghemite particles. "grain growth of the gamma-Fe_2O_3 is not carried out by sintering" collection [of the 7th ferrite summer ZEMINA lecture outlines] (1977) [19-page] This phenomenon is as the becoming statement.

[0010]JP,55-42934,B has the method of a statement, for example as a method of obtaining a high-density needlelike hematite particle substantially which is carrying out maintenance succession of the acicular shape conventionally and by which the crystalline degree was raised. Under the atmosphere which consists of heated steam and nonreducible gas, a method given in JP,55-42934,B carries out heating calcination of the needlelike hematite particle produced by carrying out heating drying of the needlelike goethite particles at 350-700 **.

[0011]

[Problem(s) to be Solved by the Invention]Although the high-density needlelike hematite particle is [in which is carrying out maintenance succession of the acicular shape, and the crystalline degree was raised] just going to be demanded most substantially now, the above -- the particle growth of a single particle occurring easily and a crystalline degree becoming what was raised more so that treatment temperature becomes an elevated temperature when based on a method given in JP,55-42934,B, but. On the other hand, particles and sintering between particles take place easily simultaneously with the particle growth of a single particle, and it becomes difficult to carry out maintenance succession of the acicular shape.

[0012]Then, this invention makes the thing for which maintenance succession of the acicular shape is carried out, and the crystalline degree was raised and which obtain a high-density needlelike hematite particle substantially a technical technical problem.

[0013]

[Means for Solving the Problem]This invention as follows can attain said technical technical problem. Namely, average length shaft length produced by this invention carrying out heating drying

of the needlelike goethite particles in a 250-400 ** temperature requirement is 0.1-0.5 micrometer, And when specific surface area by a BET adsorption method carries out water heat treatment of the aquosity solvent containing a needlelike hematite particle which is 70-150m^2/g in a 150-250 ** temperature requirement, Average length shaft length is 0.1-0.5 micrometer, and specific surface area by a BET adsorption method is a manufacturing method of acicular hematite particle powder which consists of a thing for which the shape of a needle which is 15-60m^2/g is inherited, and which obtain a high-density needlelike hematite particle substantially.

[0014]Next, terms and conditions which are in charge of this invention operation are described. Needlelike goethite particles in this invention, Oxygen containing gas is aerated for suspension containing ferrous hydroxide particles produced by mixing a well-known ferrous salt aqueous solution and an alkaline solution at temperature of 80 ** or less. It can obtain by any methods, such as a method oxidized by aerating oxygen containing gas to suspension containing $FeCO_3$ produced by making a method and a ferrous salt aqueous solution, and alkali carbonate which are oxidized react, Any particle of gestalten, such as fusiform, rice grain shape, and a spheroid, can be used as well as 0.1-0.5 micrometer of major axes, and the shape of a needle of the axial ratios (average-length shaft length: average minor axis length) 5:1-20:1. In order to raise the characteristic of magnetic particle powder made into the purpose, different species elements other than Fe(s), such as Co, nickel, Zn, aluminum, Mn, Cu, Si, etc. which are usually added, may be made to exist in a generation reaction of the above-mentioned goethite particles.

[0015]Average length shaft length produced by processed particles in this invention carrying out heating drying of the needlelike goethite particles in a 250-400 ** temperature requirement is 0.1-0.5 micrometer, and specific surface area is a needlelike hematite particle of 70-150-m^2/g. When heating dehydrating temperature is less than 250 **, it is difficult to obtain a needlelike hematite particle. When exceeding 400 **, acicular shape of a hematite particle in which sintering may occur particles and between particles will collapse. If acicular shape of a needlelike hematite particle is taken into consideration, less than 350 ** is preferred. When average length shaft length is less than 0.1 micrometer, in exceeding 0.5 micrometer, it is hard to say that maintenance succession of the acicular shape was carried out. Specific surface area of acicular hematite particle powder by which sintering was prevented particles and between particles is 50-150m^2/g.

[0016]Alkaline aqueous solutions, such as neutral water solutions, such as water, NaOH, KOH, can be used for an aquosity solvent in this invention. When an alkaline aqueous solution is used, particle growth of a single particle can be made to occur effectively at a lower temperature compared with a case where neutral water solutions, such as water, are used.

[0017]Water heat treatment in this invention can be performed by processing in a 150-250 ** temperature requirement using devices, such as autoclave. A hole remains inside a particle surface of a needlelike hematite particle, and particles, and a crystalline degree is insufficient for a case below 150 **. When exceeding 250 **, it cannot be said that weld occurred particles and between particles and maintenance succession of the acicular shape was carried out. If a crystalline degree and acicular shape are taken into consideration, 150-200 ** is preferred.

[0018]Average length shaft length is 0.1-0.5 micrometer, and specific surface area of a needlelike hematite particle after water heat treatment in this invention is 15-60m^2/g. When average length shaft length is less than 0.1 micrometer and average length shaft length exceeds 0.5 micrometer, it cannot be said that maintenance succession of the acicular shape was carried out. Specific surface area of a needlelike hematite particle to which weld was prevented particles and between particles and a crystalline degree was raised is 15-60m^2/g.

[0019]

[Function]The average length shaft length produced by the most important point carrying out heating drying of the needlelike goethite particles in this invention in a 250-400 ** temperature

requirement is 0.1-0.5 micrometer.
And when the specific surface area by a BET adsorption method carries out water heat treatment of the aquosity solvent containing the needlelike hematite particle which is 70-150m^2/g in a 150-250 ** temperature requirement. Average length shaft length is 0.1-0.5 micrometer, and the specific surface area by a BET adsorption method is the fact which has inherited the shape of a needle which is 15-60m^2/g that a high-density needlelike hematite particle can be obtained substantially.

[0020]In this invention, maintenance succession of the acicular shape is carried out, and this invention person is low temperature about the reason the crystalline degree was raised and a high-density needlelike hematite particle is obtained substantially.
I think that it is because the particle growth of the single particle occurred preferentially, without weld particles and between particles almost occurring, since it is processing in an aquosity medium.

[0021]In this invention, there are few impurities contained in the needlelike hematite particle produced by carrying out water heat treatment, such as Na^+ and SO_4^{2-}. For the reason, since particles and sintering between particles can be controlled or prevented in a subsequent heating reduction process, it has the feature of being easy to carry out maintenance succession of the acicular shape.
[0022]In this invention, this invention person contains inside particles by the ability to carry out particle growth of the single particle enough about the reason with few impurities contained in the needlelike hematite particle produced by carrying out water heat treatment, such as Na^+ and SO_4^{2-}.
I think that it will be because it is what it is easy to wash by extruding the impurity which can be hard to wash depending on the usual washing near a particle surface or the particle surface.

[0023]
[Example]Next, an example and a comparative example explain this invention. The value observed with the electron microscope showed the average length shaft length and the axial ratio (average-length shaft length: average minor axis length) in the following examples and comparative examples. Again. The value and multivolume densimeter of specific surface area according [the crystalline degree of particles] to a BET adsorption method The value which measured the density of particles with 1305 types (micro MERITIKKUSU) showed.
[0024]The pyrolysis of the needlelike alpha-FeO (OH) particle powder of the example 1 average-length shaft length of 0.35 micrometer, the axial ratio (average-length shaft length: average minor axis length) 8:1, and specific surface area ^{2}[of 48 m]/g is carried out at 320 ** among the air, It is the average length shaft length of 0.35 micrometer, and the axial ratio (average-length shaft length: average minor axis length) 8:1, and the acicular hematite particle powder (Na: 970 ppm, SO_4:680ppm) which is specific surface area 85m^2/g and the density of 4.3g/cc was obtained. Water was made to distribute the above-mentioned acicular hematite particle powder 8.0g, and it was considered as aqueous suspension with a full capacity of 100 ml. After putting this aqueous suspension into the well-closed container and carrying out water heat treatment at the temperature of 200 ** for 5 hours, settlings were filtered, and it rinsed and dried.
[0025]The obtained needlelike hematite particle is acicular hematite particle powder which is the average length shaft length of 0.35 micrometer, and the axial ratio (average-length shaft length: average minor axis length) 8:1, and is specific surface area 32m^2/g and the density of 4.6g/cc as a result of electron microscope observation.
Maintenance succession of the acicular shape was carried out, and they were the substantially high-density particles to which the crystalline degree was raised.

The impurities in this hematite particle powder were Na^+90ppm and SO_4^{2-}130ppm, and there were few impurities.

[0026]The pyrolysis of the needlelike alpha-FeO (OH) particle powder of the example 2 average-length shaft length of 0.2 micrometer, the axial ratio (average-length shaft length: average minor axis length) 7:1, and specific surface area ^{2}[of 105 m]/g is carried out at 300 ** among the air, It is the average length shaft length of 0.2 micrometer, and the axial ratio (average-length shaft length: average minor axis length) 7:1, and the acicular hematite particle powder (Na: 300 ppm, SO_4:80ppm) which is specific surface area 130m^2/g and the density of 4.2g/cc was obtained. Water was made to distribute the above-mentioned acicular hematite particle powder 8.0g, and it was considered as aqueous suspension with a full capacity of 100 ml. After putting this aqueous suspension into the well-closed container and carrying out water heat treatment at the temperature of 150 ** for 5 hours, settlings were filtered, and it rinsed and dried.

[0027]The obtained needlelike hematite particle is acicular hematite particle powder which is the average length shaft length of 0.2 micrometer, and the axial ratio (average-length shaft length: average minor axis length) 7:1, and is specific surface area 55m^2/g and the density of 4.5g/cc as a result of electron microscope observation.

Maintenance succession of the acicular shape was carried out, and they were the substantially high-density particles to which the crystalline degree was raised.

The impurities in this hematite particle powder were Na^+190ppm and SO_4^{2-}50ppm, and there were few impurities.

[0028]The pyrolysis of the needlelike alpha-FeO (OH) particle powder of the example 3 average-length shaft length of 0.4 micrometer, the axial ratio (average-length shaft length: average minor axis length) 10:1, and specific surface area ^{2}[of 20 m]/g is carried out at 340 ** among the air, It is the average length shaft length of 0.4 micrometer, and the axial ratio (average-length shaft length: average minor axis length) 10:1, and the acicular hematite particle powder (Na: 970 ppm, SO_4:4800ppm) which is specific surface area 100m^2/g and the density of 4.3g/cc was obtained. Water was made to distribute the above-mentioned acicular hematite particle powder 8.0g, and it was considered as aqueous suspension with a full capacity of 100 ml. After putting this aqueous suspension into the well-closed container and carrying out water heat treatment at the temperature of 200 ** for 5 hours, settlings were filtered, and it rinsed and dried.

[0029]The obtained needlelike hematite particle is acicular hematite particle powder which is the average length shaft length of 0.4 micrometer, and the axial ratio (average-length shaft length: average minor axis length) 10:1, and is specific surface area 18m^2/g and the density of 4.7g/cc as a result of electron microscope observation.

Maintenance succession of the acicular shape was carried out, and they were the substantially high-density particles to which the crystalline degree was raised.

The impurities in this hematite particle powder were Na^+90ppm and SO_4^{2-}730ppm, and there were few impurities.

[0030]

[Effect of the Invention]according to this invention -- the above -- maintenance succession of the acicular shape is carried out, and the substantially high-density needlelike hematite particle to which the crystalline degree was raised can be obtained as shown in the example. Are carrying out maintenance succession of the acquired acicular shape, and the substantially high-density needlelike hematite particle to which the crystalline degree was raised is used, The needlelike magnetite particle powder produced by carrying out heating reduction, heating reduction, and the needlelike maghemite particle powder produced by oxidizing are also carrying out maintenance

succession of the acicular shape, and since it is the substantially high-density magnetic particle powder in which the crystalline degree was raised, it is preferred as high density recording and magnetic particle powder for high power. Since the needlelike hematite particle in this invention has few impurities, it is easy to wash and it is advantageous on industry and economy.

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報（Ａ）**　(11)特許出願公開番号

特開平6－64927

(43)公開日　平成６年(1994)３月８日

(51)Int.Cl.[5]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｃ０１Ｇ　49/06	Ａ			
Ｈ０１Ｆ　1/11	Ｎ			

審査請求　未請求　請求項の数１（全　４　頁）

(21)出願番号　特願平3－359299

(22)出願日　平成３年(1991)12月27日

(71)出願人　000166443
戸田工業株式会社
広島県広島市西区横川新町７番１号

(72)発明者　中村　龍哉
広島県広島市中区舟入南４丁目１番２号戸田工業株式会社創造センター内

(72)発明者　本名　虎之
広島県広島市中区舟入南４丁目１番２号戸田工業株式会社創造センター内

(54)【発明の名称】　針状ヘマタイト粒子粉末の製造法

(57)【要約】

【目的】　針状形状を保持継承し、結晶性の度合が高められた実質的に高密度な針状ヘマタイト粒子を工業的に得られる製造法を提供する。

【構成】　針状ゲータイト粒子を２５０～４００℃の温度範囲で加熱脱水して得られた平均長さが０．１～０．５μｍであり、且つ、ＢＥＴ法による比表面積が７０～１５０ｍ²／ｇである針状ヘマタイト粒子を含む水性液媒を１５０～２５０℃の温度範囲で水熱処理することにより、平均長軸長さが０．１～０．５μｍであり、且つ、ＢＥＴ法による比表面積値が１５～６０ｍ²／ｇである針状ヘマタイト粒子を得る。

1

【特許請求の範囲】

【請求項１】　針状ゲータイト粒子を２５０～４００℃の温度範囲で加熱脱水して得られた平均長軸長さが０．１～０．５μｍであり、且つ、ＢＥＴ法による比表面積が７０～１５０m^2／ｇである針状ヘマタイト粒子を含む水性液媒を１５０～２５０℃の温度範囲で水熱処理することにより、平均長軸長さが０．１～０．５μｍであり、且つ、ＢＥＴ法による比表面積が１５～６０m^2／ｇである針状を継承している実質的に高密度な針状ヘマタイト粒子を得ることを特徴とする針状ヘマタイト粒子粉末の製造法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、磁気記録用磁性粒子粉末を製造する際の出発原料としての針状ヘマタイト粒子粉末の製造法に関するものであり、詳しくは、針状形状を保持継承しており、且つ、粒子表面並びに粒子内部の結晶性の度合が高められた実質的に高密度な針状ヘマタイト粒子粉末を得ることを目的とする。

【０００２】

【従来の技術】近年、磁気記録再生用機器の小型軽量化が進むにつれて磁気テープ、磁気ディスク等の磁気記録媒体に対する高性能化の必要性が益々生じてきている。すなわち、高密度記録特性、高出力特性、高感度特性、周波数特性等の諸特性の向上が要求されており、その為には、磁気記録媒体の高保磁力化と残留磁束密度Ｂｒの向上が必要である。

【０００３】磁気記録媒体の高保磁力化の為には、磁性粒子粉末が高い保磁力を有することが必要である。また、磁気記録媒体の残留磁束密度Ｂｒは、磁性粒子粉末のビヒクル中での分散性、塗膜中での配向性及び充填性に依存しており、磁性粒子粉末が針状形態であり、粒子相互間で焼結が生起しておらず、粒子表面並びに粒子内部に空孔が存在しておらず実質的に高密度であることが必要である。

【０００４】現在、磁気記録用磁性粒子粉末として主に針状マグネタイト粒子粉末や針状マグヘマイト粒子粉末が用いられている。これら磁性粒子粉末は、一般に、第一鉄塩水溶液とアルカリとを反応させて得た水溶液中の水酸化第一鉄コロイドを空気酸化し（通常、湿式反応という。）得られた針状ゲータイト粒子を空気中３００℃付近で加熱脱水して針状ヘマタイト粒子となし、さらに水素等還元性ガス中３００～４００℃で還元して針状マグネタイト粒子とし、次いでこれを空気中２００～３００℃で酸化して針状マグヘマイト粒子とすることにより得られている。

【０００５】磁性粒子粉末の保磁力Ｈｃは、次に示すような関係式により表すことができる。

$Hc = K \cdot (Nb - Na) \cdot Ms$

この関係式において、Ｋは粒子の結晶性の度合に、（Ｎｂ－Ｎａ）は粒子の形状（針状性）に、また、Ｍｓは粒子の化学的組成に関係する事項である。この関係式から明らかなように、磁性粒子粉末の保磁力の向上をはかるためには、針状ゲータイト粒子の針状形状を保持継承させることと結晶性の度合を高めることが要求される。そして、これら磁性粒子粉末の諸特性は、保磁力の向上のみならず、磁性粒子粉末のビヒクル中での分散性、塗膜中での配向性及び充填性を向上させるためにも要求される。

【０００６】従来、磁性粒子粉末の製造にあたり、前述した通りゲータイト粒子の針状形状を保持継承する為に比較的低温で加熱脱水することが行なわれている。このようにして得られた針状ヘマタイト粒子は針状ゲータイト粒子の外形を残した針状形骸粒子であるが、一方、この形骸粒子は多数の単一粒子の連結した凝集粒子からなり、該単一粒子の粒子成長が十分でないため、結晶性の度合が小さいものである。

【０００７】結晶性の度合が小さい針状ヘマタイト粒子を出発原料として用い加熱還元すると、加熱還元過程において単一粒子の粒子成長即ち、物理的変化が急激である為、単一粒子の均一な粒子成長が生起しがたく、従って、単一粒子の粒子成長が急激に生起した部分では、粒子及び粒子相互間の焼結が生起し、粒子形状がくずれやすいものとなる。

【０００８】また、針状ゲータイト粒子はＮａＯＨやＦｅＳＯ$_4$等の原料に由来するNa^+やSO_4^{2-}等の不純物を必然的に含有するが、これら不純物は加熱焼成過程において焼結を促進する為、これら不純物を多量に含む針状ゲータイト粒子を用いた場合には、加熱還元過程において粒子及び粒子相互間の焼結が一層生起しやすくなり、粒子形状がくずれやすくなる。

【０００９】尚、針状マグネタイト粒子を針状マグヘマイト粒子とする加熱酸化過程においては、単一粒子の粒子成長は生起しない。この現象は、第７回フェライト夏季ゼミナー講演概要集（１９７７年）１９頁の「γ－Fe_2O_3は焼結によって粒成長しない」なる記載の通りである。

【００１０】従来、針状形状を保持継承しており、且つ、結晶性の度合が高められた実質的に高密度な針状ヘマタイト粒子を得る方法として、例えば特公昭５５－４２９３４号公報に記載の方法がある。特公昭５５－４２９３４号公報に記載の方法は、針状ゲータイト粒子を加熱脱水して得られた針状ヘマタイト粒子を加熱水蒸気と非還元性ガスとからなる雰囲気下において３５０～７００℃で加熱焼成するものである。

【００１１】

【発明が解決しようとする課題】針状形状を保持継承しており、且つ、結晶性の度合が高められた実質的に高密度な針状ヘマタイト粒子は現在最も要求されているところであるが、前出特公昭５５－４２９３４号公報に記載

の方法による場合には、処理温度が高温になる程単一粒子の粒子成長が生起しやすく、結晶性の度合がより高められたものとなるが、一方、単一粒子の粒子成長と同時に粒子及び粒子相互間の焼結が起こりやすくなり、針状形状を保持継承することが困難となる。

【００１２】そこで、本発明は、針状形状を保持継承しており、且つ、結晶性の度合が高められた実質的に高密度な針状ヘマタイト粒子を得ることを技術的課題とする。

【００１３】

【課題を解決する為の手段】前記技術的課題は、次の通りの本発明によって達成できる。即ち、本発明は、針状ゲータイト粒子を２５０～４００℃の温度範囲で加熱脱水して得られた平均長軸長さが０．１～０．５μmであり、且つ、ＢＥＴ法による比表面積が７０～１５０m²／gである針状ヘマタイト粒子を含む水性液媒を１５０～２５０℃の温度範囲で水熱処理することにより、平均長軸長さが０．１～０．５μmであり、且つ、ＢＥＴ法による比表面積が１５～６０m²／gである針状を継承している実質的に高密度な針状ヘマタイト粒子を得ることからなる針状ヘマタイト粒子粉末の製造法である。

【００１４】次に、本発明実施にあたっての諸条件について述べる。本発明における針状ゲータイト粒子は、周知の第一鉄塩水溶液とアルカリ性溶液とを混合して得られる水酸化第一鉄粒子を含む懸濁液を８０℃以下の温度で酸素含有ガスを通気して酸化反応を行う方法及び第一鉄塩水溶液と炭酸アルカリとを反応させて得られた$FeCO_3$を含む懸濁液に酸素含有ガスを通気して酸化反応を行う方法等のいずれの方法によっても得ることができ、長軸０．１～０．５μm、軸比（平均長軸長さ：平均短軸長さ）５：１～２０：１の針状はもちろん、紡錘状、米粒状、回転楕円体等のいずれの形態の粒子をも使用することができる。上記ゲータイト粒子の生成反応においては、目的とする磁性粒子粉末の特性を向上させる為に通常添加されるＣｏ、Ｎｉ、Ｚｎ、Ａｌ、Ｍｎ、Ｃｕ、Ｓｉ等のＦｅ以外の異種元素を存在させてもよい。

【００１５】本発明における被処理粒子は、針状ゲータイト粒子を２５０～４００℃の温度範囲で加熱脱水して得られた、平均長軸長さが０．１～０．５μm、比表面積が７０～１５０m²／gの針状ヘマタイト粒子である。加熱脱水温度が２５０℃未満の場合には、針状ヘマタイト粒子を得ることが困難である。４００℃を越える場合には、粒子及び粒子相互間で焼結が生起し得られるヘマタイト粒子の針状形状が崩れてしまう。針状ヘマタイト粒子の針状形状を考慮すれば３５０℃未満が好ましい。平均長軸長さが０．１μm未満の場合、０．５μmを越える場合には、針状形状を保持継承したものとは言い難い。粒子及び粒子相互間で焼結が防止された針状ヘマタイト粒子粉末の比表面積は５０～１５０m²／gである。

【００１６】本発明における水性液媒は、水等の中性水溶液やＮａＯＨ、ＫＯＨ等のアルカリ水溶液を使用することができる。アルカリ水溶液を使用した場合には、水等の中性水溶液を使用する場合に比べ、より低い温度で効果的に単一粒子の粒子成長を生起させることができる。

【００１７】本発明における水熱処理は、オートクレーブ等の装置を使用して１５０～２５０℃の温度範囲で処理することによって行うことができる。１５０℃未満の場合には、針状ヘマタイト粒子の粒子表面並びに粒子内部に空孔が残存し、結晶性の度合が不十分である。２５０℃を越える場合には、粒子及び粒子相互間で融着が生起し針状形状を保持継承したものとは言えない。結晶性の度合並びに針状形状を考慮すれば１５０～２００℃が好ましい。

【００１８】本発明における水熱処理後の針状ヘマタイト粒子は、平均長軸長さが０．１～０．５μmであり、且つ、比表面積が１５～６０m²／gである。平均長軸長さが０．１μm未満の場合、平均長軸長さが０．５μmを越える場合には、針状形状を保持継承したものとは言えない。粒子及び粒子相互間で融着が防止され結晶性の度合が高められた針状ヘマタイト粒子の比表面積は１５～６０m²／gである。

【００１９】

【作用】本発明において最も重要な点は、針状ゲータイト粒子を２５０～４００℃の温度範囲で加熱脱水して得られた平均長軸長さが０．１～０．５μmであり、且つ、ＢＥＴ法による比表面積が７０～１５０m²／gである針状ヘマタイト粒子を含む水性液媒を１５０～２５０℃の温度範囲で水熱処理した場合には、平均長軸長さが０．１～０．５μmであり、且つ、ＢＥＴ法による比表面積が１５～６０m²／gである針状を継承している実質的に高密度な針状ヘマタイト粒子を得ることができるという事実である。

【００２０】本発明において、針状形状を保持継承しており、結晶性の度合が高められた実質的に高密度な針状ヘマタイト粒子が得られる理由について、本発明者は、低温であり、水性媒体中での処理である為に、粒子及び粒子相互間での融着がほとんど生起することなく、単一粒子の粒子成長が優先的に生起した為であると考えている。

【００２１】本発明においては、水熱処理して得られる針状ヘマタイト粒子中に含有されるNa^+やSO_4^{2-}等の不純物が少ないものである。その為、その後の加熱還元過程において粒子及び粒子相互間の焼結を抑制又は防止できるので針状形状を保持継承しやすいという特徴を有する。

【００２２】本発明において、水熱処理して得られる針状ヘマタイト粒子中に含有されるNa^+やSO_4^{2-}等の不純物が少ない理由について、本発明者は、単一粒子を

十分粒子成長させることができることによって、粒子内部に含有されており、通常の洗浄によっては洗浄できにくい不純物が粒子表面又は粒子表面近傍に押し出されることによって洗浄しやすいものになっているためであろうと考えている。

【００２３】

【実施例】次に、実施例並びに比較例により本発明を説明する。尚、以下の実施例並びに比較例における平均長軸長さ及び軸比（平均長軸長さ：平均短軸長さ）は電子顕微鏡により観察した値で示した。また。粒子の結晶性の度合は、ＢＥＴ法による比表面積の値とマルチボリューム密度計　１３０５型（マイクロメリティックス社）によって粒子の密度を測定した値で示した。

【００２４】実施例１

平均長軸長さ０．３５μｍ、軸比（平均長軸長さ：平均短軸長さ）８：１、比表面積４８ｍ²／ｇの針状α－ＦｅＯ（ＯＨ）粒子粉末を空気中３２０℃にて熱分解して、平均長軸長さ０．３５μｍ、軸比（平均長軸長さ：平均短軸長さ）８：１であって、比表面積８５ｍ²／ｇ、密度４．３ｇ／ｃｃである針状ヘマタイト粒子粉末（Ｎａ：９７０ｐｐｍ、SO_4：６８０ｐｐｍ）を得た。上記針状ヘマタイト粒子粉末８．０ｇを水に分散させて、全容量１００ｍｌの水懸濁液とした。この水懸濁液を、密閉容器に入れ、温度２００℃にて５時間水熱処理した後、沈澱物を濾別、水洗、乾燥した。

【００２５】得られた針状ヘマタイト粒子は、電子顕微鏡観察の結果、平均長軸長さ０．３５μｍ、軸比（平均長軸長さ：平均短軸長さ）８：１であって、比表面積３２ｍ²／ｇ、密度４．６ｇ／ｃｃである針状ヘマタイト粒子粉末であり、針状形状を保持継承しており、結晶性の度合が高められた実質的に高密度の粒子であった。また、このヘマタイト粒子粉末中の不純物はNa^+　９０ｐｐｍ、SO_4^{2-}　１３０ｐｐｍであり、不純物が少ないものであった。

【００２６】実施例２

平均長軸長さ０．２μｍ、軸比（平均長軸長さ：平均短軸長さ）７：１、比表面積１０５ｍ²／ｇの針状α－ＦｅＯ（ＯＨ）粒子粉末を空気中３００℃にて熱分解して、平均長軸長さ０．２μｍ、軸比（平均長軸長さ：平均短軸長さ）７：１であって、比表面積１３０ｍ²／ｇ、密度４．２ｇ／ｃｃである針状ヘマタイト粒子粉末（Ｎａ：３００ｐｐｍ、SO_4：８０ｐｐｍ）を得た。上記針状ヘマタイト粒子粉末８．０ｇを水に分散させて、全容量１００ｍｌの水懸濁液とした。この水懸濁液を、密閉容器に入れ、温度１５０℃にて５時間水熱処理した後、沈澱物を濾別、水洗、乾燥した。

【００２７】得られた針状ヘマタイト粒子は、電子顕微鏡観察の結果、平均長軸長さ０．２μｍ、軸比（平均長軸長さ：平均短軸長さ）７：１であって、比表面積５５ｍ²／ｇ、密度４．５ｇ／ｃｃである針状ヘマタイト粒子粉末であり、針状形状を保持継承しており、結晶性の度合が高められた実質的に高密度の粒子であった。また、このヘマタイト粒子粉末中の不純物はNa^+　１９０ｐｐｍ、SO_4^{2-}　５０ｐｐｍであり、不純物が少ないものであった。

【００２８】実施例３

平均長軸長さ０．４μｍ、軸比（平均長軸長さ：平均短軸長さ）１０：１、比表面積２０ｍ²／ｇの針状α－ＦｅＯ（ＯＨ）粒子粉末を空気中３４０℃にて熱分解して、平均長軸長さ０．４μｍ、軸比（平均長軸長さ：平均短軸長さ）１０：１であって、比表面積１００ｍ²／ｇ、密度４．３ｇ／ｃｃである針状ヘマタイト粒子粉末（Ｎａ：９７０ｐｐｍ、SO_4：４８００ｐｐｍ）を得た。上記針状ヘマタイト粒子粉末８．０ｇを水に分散させて、全容量１００ｍｌの水懸濁液とした。この水懸濁液を、密閉容器に入れ、温度２００℃にて５時間水熱処理した後、沈澱物を濾別、水洗、乾燥した。

【００２９】得られた針状ヘマタイト粒子は、電子顕微鏡観察の結果、平均長軸長さ０．４μｍ、軸比（平均長軸長さ：平均短軸長さ）１０：１であって、比表面積１８ｍ²／ｇ、密度４．７ｇ／ｃｃである針状ヘマタイト粒子粉末であり、針状形状を保持継承しており、結晶性の度合が高められた実質的に高密度の粒子であった。また、このヘマタイト粒子粉末中の不純物はNa^+　９０ｐｐｍ、SO_4^{2-}　７３０ｐｐｍであり、不純物が少ないものであった。

【００３０】

【発明の効果】本発明によれば、前出実施例に示した通り、針状形状を保持継承しており、結晶性の度合が高められた実質的に高密度な針状ヘマタイト粒子を得ることができる。得られた針状形状を保持継承しており、結晶性の度合が高められた実質的に高密度な針状ヘマタイト粒子を用いて、加熱還元して得られた針状マグネタイト粒子粉末、加熱還元、酸化して得られた針状マグヘマイト粒子粉末もまた、針状形状を保持継承しており、結晶性の度合が高められた実質的に高密度な磁性粒子粉末であるので、高密度記録、高出力用磁性粒子粉末として好適である。尚、本発明における針状ヘマタイト粒子は不純物が少ないものであるから、洗浄が容易であり、工業上、経済上有利である。